

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
5 February 2004 (05.02.2004)

PCT

(10) International Publication Number  
WO 2004/011693 A1

(51) International Patent Classification<sup>7</sup>: C23C 16/44, C30B 25/14

(21) International Application Number: PCT/US2003/022804

(22) International Filing Date: 21 July 2003 (21.07.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data: 10/208,314 29 July 2002 (29.07.2002) US

(71) Applicant: MICRON TECHNOLOGY, INC. [US/US]; 8000 South Federal Way, Boise, ID 83716 (US).

(72) Inventors: CASTROVILLO, Paul, J.; 1814 North Phillipi, Boise, ID 83706 (US). BASCERI, Cem; 314 East Iowa Drive, Boise, ID 83706 (US). DERDERIAN, Garo, J.; 6184 South. Schooner Place, Boise, ID 83706 (US). SANDHU, Gurtej, S.; 2964 East Parkriver Drive, Boise, ID 83706 (US).

(74) Agents: MATKIN, Mark, S. et al.; 601 West First Avenue, 1300 Spokane, WA 99201-3828 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.

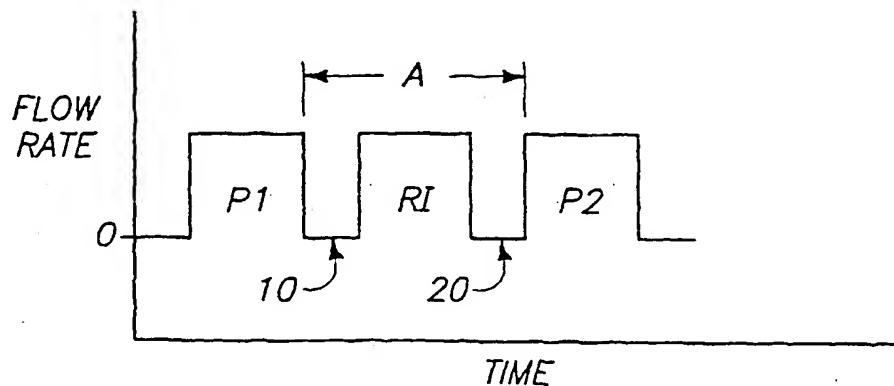
(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report  
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: ATOMIC DEPOSITION LAYER METHODS



WO 2004/011693 A1

(57) Abstract: An atomic layer deposition method includes positioning a semiconductor substrate within an atomic layer deposition chamber. A first precursor gas is flowed to the substrate within the atomic layer deposition chamber effective to form a first monolayer on the substrate. After forming the first monolayer, a reactive intermediate gas is flowed to the substrate within the deposition chamber. The reactive intermediate gas is capable of reaction with an intermediate reaction by-product from the first precursor flowing under conditions of the reactive intermediate gas flowing. After flowing the reactive intermediate gas, a second precursor gas is flowed to the substrate within the deposition chamber effective to form a second monolayer on the first monolayer. Other aspects and implementations are contemplated.

DESCRIPTION

## ATOMIC DEPOSITION LAYER METHODS

Technical Field

5 This invention relates to atomic layer deposition methods.

Background Art

Atomic layer deposition (ALD) involves the deposition of successive monolayers over a substrate within a deposition chamber typically maintained at subatmospheric pressure. An exemplary such method includes feeding a single 10 vaporized precursor to a deposition chamber effective to form a first monolayer over a substrate received therein. Thereafter, the flow of the first deposition precursor is ceased and an inert purge gas is flowed through the chamber effective to remove any remaining first precursor which is not adhering to the substrate from the chamber. Subsequently, a second vapor precursor different from the first is flowed 15 to the chamber effective to form a second monolayer on/with the first monolayer. The second monolayer might react with the first monolayer. Additional precursors can form successive monolayers, or the above process can be repeated until a desired thickness and composition layer has been formed over the substrate.

It is a desired intent or effect of the purging to remove gas molecules that 20 have not adsorbed to the substrate or unreacted gas or reaction by-products from the chamber to provide a clean reactive surface on the substrate for the subsequent precursor. In the context of this document, a reaction by-product is any substance (whether gas, liquid, solid or mixture thereof) which results from reaction of any deposition precursor flowing to the chamber and that is not desired to be deposited 25 on the substrate. Further in the context of this document, an intermediate reaction by-product or reaction intermediate by-product is a reaction by-product formed by less than complete reaction of a precursor to form a desired monolayer on the substrate. Where there is a great degree of varying topography and/or there are high aspect ratio features on the substrate, it can be difficult to move the unreacted 30 gases or reaction by-products from deep within openings for ultimate removal from the chamber. Further, certain reaction by-products, particularly intermediate reaction by-products, may not be gaseous and may not completely react to form gaseous reaction by-products in the typical short precursor pulse times. Accordingly, the 35 purge gas pulse may not be effective or sufficient in removing such intermediate reaction by-products from the substrate and chamber.

For example, consider that in an atomic layer deposition of titanium nitride using  $TiCl_4$  and  $NH_3$ , the desired deposition product is  $TiN$  with  $HCl$  gas being the desired principle gaseous by-product. Consider also that there might be reaction intermediate by-products which might, even if gaseous, be difficult to remove from 5 substrate openings. Further, if certain reaction intermediate by-products are solid and/or liquid phase prior to  $HCl$  formation, complete removal can be even more problematic where less than complete reaction to  $TiN$  and  $HCl$  occurs.

Consider also the atomic layer deposition of  $Al_2O_3$  using trimethylaluminum (TMA) and ozone as alternating deposition precursors. Apparently in such 10 deposition, achieving an effective ozone precursor feed can be somewhat of a challenge due to the limited lifetime of ozone within the chamber. Specifically, an ozone molecule is in an inherently unstable, reactive form of oxygen which can rapidly dissociate and/or combine with another ozone molecule to form three  $O_2$  molecules. Regardless, a desired goal in the ozone feed is adsorption of oxygen 15 atoms from the  $O_3$  to the surface of the substrate with  $O_2$  as the reaction by-product which is driven off. Of course, the  $O_2$  which forms deep within openings on the substrate has to be removed therefrom while more  $O_3$  needs to get into the openings to form a complete monolayer of oxygen atoms adhering to the substrate. In other words, the  $O_2$  which forms is trying to get out while more  $O_3$  20 is trying to get in.

While the invention was motivated in addressing the above issues and improving upon the above-described drawbacks, it is in no way so limited. The invention is only limited by the accompanying claims as literally worded (without interpretative or other limiting reference to the above background art description, 25 remaining portions of the specification or the drawings) and in accordance with the doctrine of equivalents.

#### Summary

The invention includes atomic layer deposition methods. In one implementation, an atomic layer deposition method includes positioning a 30 semiconductor substrate within an atomic layer deposition chamber. A first precursor gas is flowed to the substrate within the atomic layer deposition chamber effective to form a first monolayer on the substrate. After forming the first monolayer, a reactive intermediate gas is flowed to the substrate within the deposition chamber. The reactive intermediate gas is capable of reaction with an intermediate reaction 35 by-product from the first precursor flowing under conditions of the reactive intermediate gas flowing. After flowing the reactive intermediate gas, a second

precursor gas is flowed to the substrate within the deposition chamber effective to form a second monolayer on the first monolayer.

In one implementation, an atomic layer deposition method includes positioning a semiconductor substrate within an atomic layer deposition chamber. A first precursor gas is flowed to the substrate within the atomic layer deposition chamber effective to form a first monolayer on the substrate. After forming the first monolayer, a plurality of inert purge gas pulses are flowed to the substrate within the deposition chamber, with the plurality of inert purge gas pulses including at least some period of time between at least two adjacent inert purge gas pulses when no gas is fed to the chamber. After the plurality of inert purge gas pulses, a second precursor gas is flowed to the substrate within the deposition chamber effective to form a second monolayer on the first monolayer.

Other aspects and implementations are contemplated.

#### Brief Description of the Drawings

Preferred embodiments of the invention are described below with reference to the following accompanying drawings.

Fig. 1 is a diagrammatic depiction of flow versus time of one atomic layer deposition process in accordance with an aspect of the invention.

Fig. 2 is a diagrammatic depiction of flow versus time of one atomic layer deposition process in accordance with an aspect of the invention.

Fig. 3 is a diagrammatic depiction of flow versus time of one atomic layer deposition process in accordance with an aspect of the invention.

Fig. 4 is a diagrammatic depiction of flow versus time of one atomic layer deposition process in accordance with an aspect of the invention.

Fig. 5 is a diagrammatic depiction of flow versus time of one atomic layer deposition process in accordance with an aspect of the invention.

#### Best Modes for Carrying Out the Invention and Disclosure of Invention

An atomic layer deposition method in accordance with an aspect of the invention includes positioning a semiconductor substrate within an atomic layer deposition chamber. In the context of this document, the term "semiconductor substrate" or "semiconductive substrate" is defined to mean any construction comprising semiconductive material, including, but not limited to, bulk semiconductive materials such as a semiconductive wafer (either alone or in assemblies comprising other materials thereon), and semiconductive material layers (either alone or in assemblies comprising other materials). The term "substrate" refers to any supporting structure, including, but not limited to, the semiconductive substrates described above.

A first precursor gas is flowed to the substrate within the atomic layer deposition chamber effective to form a first monolayer on the substrate. Any first precursor gas is contemplated, whether existing or yet-to-be developed. By way of example only, where a desired ultimate deposition product or layer is TiN, an 5 example first precursor could be either  $TiCl_4$  or  $NH_3$ . Further by way of example only, where the ultimate layer or product being formed is to be  $Al_2O_3$ , exemplary first precursor gases include trimethylaluminum and ozone. By way of example only, an exemplary first monolayer utilizing  $TiCl_4$  would include titanium or a titanium complex, whereas with respect to  $NH_3$  such would at least include nitrogen. 10 With respect to trimethylaluminum, the first monolayer would include an aluminum complex, and with ozone typically adhered oxygen atoms. Any suitable temperature, pressure, flow rate or other operating parameters, with or without plasma, can of course be selected and optimized by the artisan with no particular set of the same being preferred or constituting a part of the invention.

15 After forming the first monolayer, a reactive intermediate gas is flowed to the substrate within the deposition chamber. In the context of this document, a "reactive intermediate gas" is one which is capable of reaction with an intermediate reaction by-product from the first precursor flowing under conditions of the reactive intermediate gas flowing. Further and preferably, the reactive intermediate gas is 20 not capable of reaction with either the first monolayer under the reactive intermediate gas flowing conditions, nor capable of reaction with any of the first precursor which might be remaining in the reactor under the reactive intermediate gas flowing conditions. Further in one preferred embodiment, the reactive intermediate gas is not capable of reaction with, and does not react with, any 25 exposed portion of the substrate under the reactive intermediate gas flowing conditions during such flowing of the reactive intermediate gas.

In one aspect, the invention contemplates reactive intermediate gas flowing regardless of whether any intermediate reaction by-product actually forms during the first precursor gas flowing. Further in another preferred aspect, the invention also 30 contemplates forming some intermediate reaction by-product during the first precursor gas flowing, and then reacting the reactive intermediate gas with the intermediate reaction by-product during the reactive intermediate gas flowing.

The conditions (i.e., temperature, pressure, flow rate, etc.) of the reactive intermediate gas flowing to the substrate within the deposition chamber can be 35 optimized by the artisan and are not otherwise particularly germane or preferred to any aspect of the invention. By way of example only, such conditions might be

the same as or different from any of a first precursor gas flow, a second precursor gas flow and/or inert purge gas flow. In one preferred aspect, the reactive gas flowing is plasma enhanced for example by one or both of plasma generation within the chamber and plasma generation remote of the chamber.

5 The particular reactive intermediate gas selected, whether a single constituent or a mixture of constituents, will depend as a minimum upon at least one intermediate reaction by-product from the first precursor flowing with which the reactive intermediate gas would be capable of reaction under conditions of the reactive intermediate gas flowing. By way of example only, two possible 10 intermediate reactive gas components include  $\text{Cl}_2$  and  $\text{H}_2$ , and which would be expected to be particularly useful with one or both of  $\text{TiCl}_4$  and  $\text{NH}_3$  precursors. For example, with respect to  $\text{TiCl}_4$  and  $\text{NH}_3$  reaction by-products, such might include  $\text{TiCl}_2$ ,  $\text{TiCl}_3$  and  $\text{NH}_3$  complexes.  $\text{Cl}_2$  and/or  $\text{H}_2$  could be provided to the reactor for availability to react with these reaction by-products to facilitate their 15 conversion to the ultimate stoichiometric equation reaction by-product (i.e., gaseous  $\text{HCl}$ ), or react to form some other product which might be more easily swept from the reactor either by the flowing reactive intermediate gas, by some other gas or by no other gas flowing.

After flowing the reactive intermediate gas, a second precursor gas is flowed 20 to the substrate within the deposition chamber effective to form a second monolayer on the first monolayer, with "on" of course meaning in at least partial direct physical contact with the first monolayer. The second precursor is typically and preferably different in composition from the first precursor. Further preferably, the reactive intermediate gas is chosen to not be capable of reaction with the second 25 precursor under the reactive intermediate gas flowing conditions. By way of example only, exemplary second precursors include any of the above  $\text{TiCl}_4$ ,  $\text{NH}_3$ , TMA and ozone in the respective exemplary deposition reactions referred to above. In accordance with any existing or yet-to-be developed atomic layer deposition method, the formed second monolayer might combine with the first monolayer to 30 thereby inherently form a desired deposition product (i.e.,  $\text{TiN}$  or  $\text{Al}_2\text{O}_3$ , with the above referred to respective precursors), or to form a second monolayer that does not necessarily inherently react with the underlying first monolayer. The particular conditions of the flowing of the second precursor can be optimized by the artisan, of course, and do not constitute a material or preferred aspect of the inventions 35 disclosed herein.

By way of example only, Fig. 1 depicts an exemplary plot of flow rate versus time of but one process in accordance with one aspect of the invention. In Fig. 1, P1 refers to a time period during which a first precursor flows to the chamber; RI refers to a time period during which a reactive intermediate gas flows 5 to the substrate; and P2 refers to a time period during which a second precursor flows to the chamber. Accordingly, Fig. 1 depicts a preferred embodiment wherein the first precursor gas flowing, the reactive intermediate gas flowing and the second precursor gas flowing collectively comprise multiple time-spaced gas pulses to the substrate within the deposition chamber. In one preferred embodiment, there is 10 some period of time between the first precursor gas flowing and the reactive intermediate gas flowing during which no gas is fed to the chamber, and as illustrated by example only with respect to location 10. Further in one preferred embodiment, there is a period of time between the reactive intermediate gas flowing and the second precursor gas flowing during which no gas is fed to the chamber 15 and as, by way of example only, is indicated with the numeral 20. The particular length and rates of the respective flowings, and times therebetween, can be optimized by the artisan, of course, and do not constitute a material or preferred aspect of the inventions disclosed herein. Further, a first precursor gas pulse and a second precursor gas pulse are only stated or related temporally, of course, and 20 not necessarily that the first stated precursor gas flowing or pulsing is a first ever precursor flowing to the chamber. Likewise and accordingly depending upon which portion of a time line much like the figures to which one is looking, second precursor gas pulses can be considered as first precursor gas pulses, and vice versa.

Fig. 1 also depicts one embodiment whereby there exists a total period of 25 time "A" between first precursor feeding P1 and second precursor feeding P2. Total period of time A is characterized by no gas being fed to the chamber during said total period but for said reactive intermediate gas flowing RI. However, the invention also contemplates other gas flowings intermediate a first precursor feeding and a second precursor feeding. By way of example only, such are depicted in 30 Figs. 2-5 in certain aspects. Fig. 2 depicts the flowing of an inert purge gas in the form of an inert gas pulse (IN) which is time-spaced from all other gas flowings to the substrate within the deposition chamber after flowing reactive intermediate gas pulse RI. Accordingly by way of example only, the exemplary diagrammatic Fig. 2 processing depicts a total period of time "B" between first 35 precursor feeding P1 and second precursor feeding P2 having more than just the reactive intermediate gas flow RI.

Fig. 3 depicts another embodiment similar to Fig. 2, but for the reversal of the sequence of the inert gas pulsing and reactive intermediate gas pulsing between the first and second precursor flows.

Fig. 4 depicts another exemplary atomic layer deposition method which, in certain aspects, is not dependent upon any reactive intermediate gas flowing as described above. Specifically and by way of example only, Fig. 4 depicts, after the forming of a first monolayer from a precursor P1 flowing, a plurality of inert purge gas pulses IN flowing to the substrate within the deposition chamber, with such inert purge gas pulses being time-spaced such that there is at least some period of time (i.e., a period 50) between at least two adjacent inert purge gas pulses IN when no gas is fed to the chamber. By way of example only and in no way of limitation, such multiple, time-spaced inert purge gas pulses might facilitate the removal of reaction intermediate by-products, particularly from within high aspect ratio openings on the substrate. In the context of this document, "two adjacent inert purge gas pulses" refers to two inert purge gas pulses that have no other purge gas pulse therebetween. The phase "two immediately adjacent inert purge gas pulses" refers to two inert purge gas pulses that have no gas pulse therebetween.

Fig. 4 depicts an exemplary embodiment wherein the plurality of inert purge gas pulses intermediate the first and second precursor flowings is two in number. Of course, the number of inert purge gas pulses to the chamber might be more than two in number. Further, the inert purge gas pulses might be of the same or common inert purge gas composition within the illustrated or all of the plurality of purge gas pulses, or be of some degree of varying composition. Fig. 4 also depicts but one preferred embodiment wherein there is a total period of time "C" between the first precursor feeding and the second precursor feeding. Total period of time C is characterized by no gas being fed to the chamber during such total period but for the plurality of inert purge gas pulses IN. Further considered and by way of example only, the depicted exemplary Fig. 4 processing illustrates a total period of time "D" between the illustrated two immediately adjacent inert purge gas pulses IN. Such total period of time D is characterized by no gas being fed to the chamber during such total period D.

By way of example only, Fig. 5 illustrates an exemplary alternate process having a total period of time D' between the two adjacent inert purge gas pulses IN which is characterized by or includes a reactive intermediate gas flowing RI to the substrate within the deposition chamber, for example in accordance with the

first-described embodiments. Accordingly and by way of example only, Fig. 5 also depicts in accordance with the first-described embodiments, the flowing of multiple time-spaced inert purge gas pulses IN to the substrate within the deposition chamber intermediate the first precursor flowing and the second precursor flowing. Of course, the IN and RI pulses could be ordered in any conceivable manner between the first and second precursor flowings, as well as other inert gas pulses, reactive intermediate gas pulses or other gas pulses added between the first and second precursor flows P1 and P2, respectively. Further, any processing of the substrate could occur, either before or after the Figs. 1-5 depicted processings, and the depicted processings would typically and preferably be repeated as selected by the artisan to achieve a desired thickness deposition by atomic layer deposition on the substrate.

The invention might have particular applicability to formation of hemispherical grain polysilicon container capacitors formed within high aspect ratio openings, but is in no way so limited.

In compliance with the statute, the invention has been described in language more or less specific as to structural and methodical features. It is to be understood, however, that the invention is not limited to the specific features shown and described, since the means herein disclosed comprise preferred forms of putting the invention into effect. The invention is, therefore, claimed in any of its forms or modifications within the proper scope of the appended claims appropriately interpreted in accordance with the doctrine of equivalents.

CLAIMS

1. An atomic layer deposition method, comprising:  
positioning a semiconductor substrate within an atomic layer deposition  
5 chamber;

flowing a first precursor gas to the substrate within the atomic layer deposition chamber effective to form a first monolayer on the substrate;

10 after forming the first monolayer, flowing a reactive intermediate gas to the substrate within the deposition chamber, the reactive intermediate gas being capable of reaction with an intermediate reaction by-product from the first precursor flowing under conditions of the reactive intermediate gas flowing; and

after flowing the reactive intermediate gas, flowing a second precursor gas to the substrate within the deposition chamber effective to form a second monolayer on the first monolayer.

15

2. The method of claim 1 comprising forming the intermediate reaction by-product during the first precursor gas flowing and reacting the reactive intermediate gas with the intermediate reaction by-product during the reactive intermediate gas flowing.

20

3. The method of claim 1 wherein the second precursor is different in composition from the first precursor.

4. The method of claim 1 wherein there is a period of time between  
25 the first precursor gas flowing and the reactive intermediate gas flowing during which no gas is fed to the chamber.

5. The method of claim 1 wherein there is a period of time between  
30 the reactive intermediate gas flowing and the second precursor gas flowing during which no gas is fed to the chamber.

6. The method of claim 1 wherein,

there is a first period of time between the first precursor gas flowing and the reactive intermediate gas flowing during which no gas is fed to the chamber; and

5 there is a second period of time between the reactive intermediate gas flowing and the second precursor gas flowing during which no gas is fed to the chamber.

7. The method of claim 1 wherein the reactive intermediate gas  
10 comprises  $\text{Cl}_2$ .

8. The method of claim 1 wherein the reactive intermediate gas comprises  $\text{H}_2$ .

15 9. The method of claim 1 wherein the reactive intermediate gas is not capable of reaction with the first precursor under said conditions.

10. The method of claim 1 wherein the reactive intermediate gas is not capable of reaction with the second precursor under said conditions.

20

11. The method of claim 1 wherein the first precursor comprises  $\text{TiCl}_4$ , the second precursor comprises  $\text{NH}_3$ , and the reactive intermediate gas comprises at least one of  $\text{H}_2$  and  $\text{Cl}_2$ .

25 12. The method of claim 1 wherein the first precursor comprises  $\text{NH}_3$ , the second precursor comprises  $\text{TiCl}_4$ , and the reactive intermediate gas comprises at least one of  $\text{H}_2$  and  $\text{Cl}_2$ .

13. The method of claim 1 comprising flowing multiple time spaced inert  
30 purge gas pulses to the substrate within the deposition chamber intermediate the first precursor flowing and the second precursor flowing.

14. The method of claim 1 wherein the first precursor gas flowing, the reactive intermediate gas flowing and the second precursor gas flowing collectively  
35 comprise multiple time spaced gas pulses to the substrate within the deposition chamber.

15. The method of claim 14 comprising a total period of time between the first precursor feeding and the second precursor feeding, the total period of time being characterized by no gas being fed to the chamber during said total period but for said reactive intermediate gas flowing.

5

16. The method of claim 1 wherein the reactive intermediate gas flowing is plasma enhanced.

17. The method of claim 1 wherein the reactive intermediate gas flowing 10 is plasma enhanced by plasma generation within the chamber.

18. The method of claim 1 wherein the reactive intermediate gas flowing is plasma enhanced by plasma generation remote of the chamber.

15

19. An atomic layer deposition method, comprising:  
positioning a semiconductor substrate within an atomic layer deposition chamber;  
flowing a first precursor gas to the substrate within the atomic layer deposition chamber effective to form a first monolayer on the substrate;  
20 after forming the first monolayer, flowing a reactive intermediate gas to the substrate within the deposition chamber, the reactive intermediate gas being capable of reaction with an intermediate reaction by-product from the first precursor flowing under conditions of the reactive intermediate gas flowing and not being capable of reaction with the first monolayer under said conditions; and  
25 after flowing the reactive intermediate gas, flowing a second precursor gas different in composition from the first precursor gas to the substrate within the deposition chamber effective to form a second monolayer on the first monolayer.

20. The method of claim 19 wherein the reactive intermediate gas is not 30 capable of reaction with, and does not react with, any exposed portion of the substrate under said conditions during the flowing of the reactive intermediate gas.

21. The method of claim 19 wherein the reactive intermediate gas is not capable of reaction with the first precursor under said conditions.

22. The method of claim 19 wherein the reactive intermediate gas is not capable of reaction with the second precursor under said conditions.

23. The method of claim 19 comprising forming the intermediate reaction by-product during the first precursor gas flowing and reacting the reactive intermediate gas with the intermediate reaction by-product during the reactive intermediate gas flowing.

24. The method of claim 19 comprising forming the intermediate reaction by-product during the first precursor gas flowing and reacting the reactive intermediate gas with the intermediate reaction by-product during the reactive intermediate gas flowing; and

wherein the reactive intermediate gas is not capable of reaction with, and does not react with, any exposed portion of the substrate under said conditions during the flowing of the reactive intermediate gas.

25. The method of claim 24 wherein the reactive intermediate gas is not capable of reaction with the first precursor under said conditions.

26. The method of claim 24 wherein the reactive intermediate gas is not capable of reaction with the second precursor under said conditions.

27. The method of claim 24 wherein the reactive intermediate gas is not capable of reaction with either of the first precursor or the second precursor under said conditions.

28. The method of claim 24 comprising flowing multiple time spaced inert purge gas pulses to the substrate within the deposition chamber intermediate the first precursor flowing and the second precursor flowing.

29. The method of claim 24 wherein the first precursor gas flowing, the reactive intermediate gas flowing and the second precursor gas flowing collectively comprise multiple time spaced gas pulses to the substrate within the deposition chamber.

30. An atomic layer deposition method, comprising:  
positioning a semiconductor substrate within an atomic layer deposition chamber;  
flowing a first precursor gas to the substrate within the atomic layer deposition chamber effective to form a first monolayer on the substrate;  
after forming the first monolayer, flowing a reactive intermediate gas to the substrate within the deposition chamber, the reactive intermediate gas being capable of reaction with an intermediate reaction by-product from the first precursor flowing under conditions of the reactive intermediate gas flowing;  
10 after flowing the reactive intermediate gas, flowing an inert purge gas to the substrate within the deposition chamber; and  
after flowing the inert purge gas, flowing a second precursor gas to the substrate within the deposition chamber effective to form a second monolayer on the first monolayer.

15

31. The method of claim 30 wherein the reactive intermediate gas is not capable of reaction with, and does not react with, any exposed portion of the substrate under said conditions during the flowing of the reactive intermediate gas.

20 32. The method of claim 30 wherein the reactive intermediate gas is not capable of reaction with the first precursor under said conditions.

25

33. The method of claim 30 wherein the reactive intermediate gas is not capable of reaction with the second precursor under said conditions.

30 34. The method of claim 30 comprising forming the intermediate reaction by-product during the first precursor gas flowing and reacting the reactive intermediate gas with the intermediate reaction by-product during the reactive intermediate gas flowing.

35. The method of claim 30 wherein the inert purge gas flowing is as a pulse which is time spaced from all other gas flowings, and comprising conducting multiple inert purge gas pulses intermediate the first precursor flowing and the second precursor flowing.

35

36. The method of claim 30 wherein the first precursor gas flowing, the reactive intermediate gas flowing, the inert gas flowing and the second precursor gas flowing collectively comprise multiple time spaced gas pulses to the substrate within the deposition chamber.

5

37. An atomic layer deposition method, comprising:  
positioning a semiconductor substrate within an atomic layer deposition chamber;

10 flowing a first precursor gas to the substrate within the atomic layer deposition chamber effective to form a first monolayer on the substrate;

after forming the first monolayer, flowing an inert purge gas to the substrate within the deposition chamber;

15 after flowing the reactive intermediate gas, flowing a reactive intermediate gas to the substrate within the deposition chamber, the reactive intermediate gas being capable of reaction with an intermediate reaction by-product from the first precursor flowing under conditions of the reactive intermediate gas flowing; and

after flowing the inert purge gas, flowing a second precursor gas to the substrate within the deposition chamber effective to form a second monolayer on the first monolayer.

20

38. The method of claim 37 wherein the reactive intermediate gas is not capable of reaction with, and does not react with, any exposed portion of the substrate under said conditions during the flowing of the reactive intermediate gas.

25

39. The method of claim 37 wherein the reactive intermediate gas is not capable of reaction with the first precursor under said conditions.

40. The method of claim 37 wherein the reactive intermediate gas is not capable of reaction with the second precursor under said conditions.

30

41. The method of claim 37 comprising forming the intermediate reaction by-product during the first precursor gas flowing and reacting the reactive intermediate gas with the intermediate reaction by-product during the reactive intermediate gas flowing.

35

42. The method of claim 37 wherein the inert purge gas flowing is as a pulse which is time spaced from all other gas flowings, and comprising conducting multiple inert purge gas pulses intermediate the first precursor flowing and the second precursor flowing.

5

43. The method of claim 37 wherein the first precursor gas flowing, the inert gas flowing, the reactive intermediate gas flowing, and the second precursor gas flowing collectively comprise multiple time spaced gas pulses to the substrate within the deposition chamber.

10

44. An atomic layer deposition method, comprising:

positioning a semiconductor substrate within an atomic layer deposition chamber;

flowing a first precursor gas to the substrate within the atomic layer deposition chamber effective to form a first monolayer on the substrate;

after forming the first monolayer, flowing a plurality of inert purge gas pulses to the substrate within the deposition chamber, the plurality of inert purge gas pulses comprising at least some period of time between at least two adjacent inert purge gas pulses when no gas is fed to the chamber; and

20 after said plurality of inert purge gas pulses, flowing a second precursor gas to the substrate within the deposition chamber effective to form a second monolayer on the first monolayer.

45. The method of claim 44 wherein the plurality is two.

25

46. The method of claim 44 wherein the plurality is more than two.

47. The method of claim 44 wherein the plurality is characterized by a common inert purge gas composition in all of said plurality.

30

48. The method of claim 44 comprising a total period of time between the first precursor feeding and the second precursor feeding, the total period of time being characterized by no gas being fed to the chamber during said total period but for said plurality of inert purge gas pulses.

35

49. The method of claim 44 comprising a total period of time between said two adjacent inert purge gas pulses, the total period of time being characterized by no gas being fed to the chamber during said total period.

5 50. The method of claim 44 comprising a total period of time between said two adjacent inert purge gas pulses, the total period of time comprising flowing a reactive intermediate gas to the substrate within the deposition chamber, the reactive intermediate gas being capable of reaction with an intermediate reaction by-product from the first precursor flowing under conditions of the reactive  
10 intermediate gas flowing.

51. The method of claim 50 wherein the reactive intermediate gas is not capable of reaction with, and does not react with, any exposed portion of the substrate under said conditions during the flowing of the reactive intermediate gas.

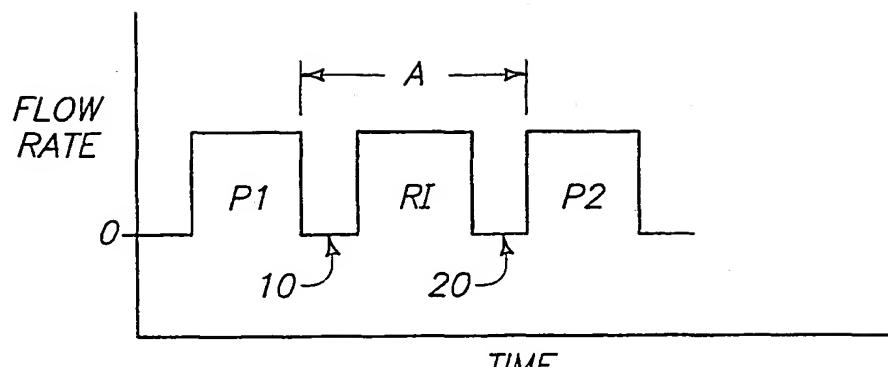
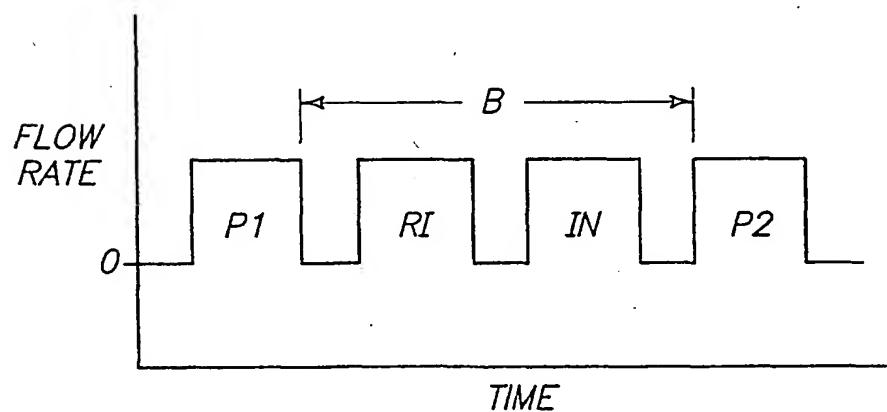
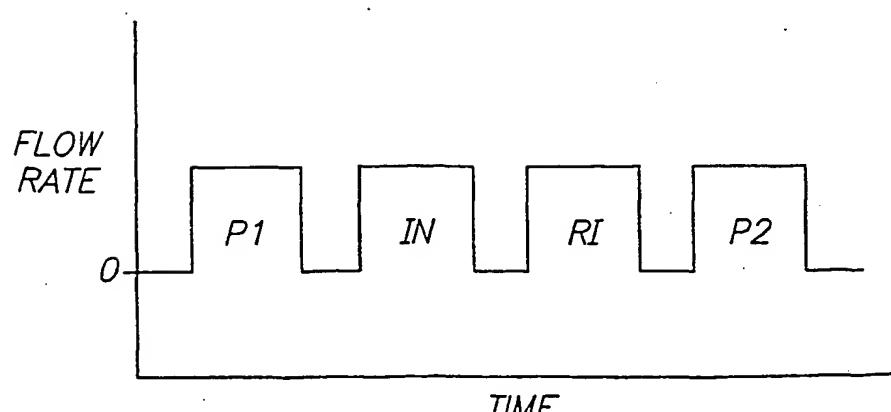
15 52. The method of claim 50 comprising forming the intermediate reaction by-product during the first precursor gas flowing and reacting the reactive intermediate gas with the intermediate reaction by-product during the reactive intermediate gas flowing.

20 53. The method of claim 50 comprising forming the intermediate reaction by-product during the first precursor gas flowing and reacting the reactive intermediate gas with the intermediate reaction by-product during the reactive intermediate gas flowing; and

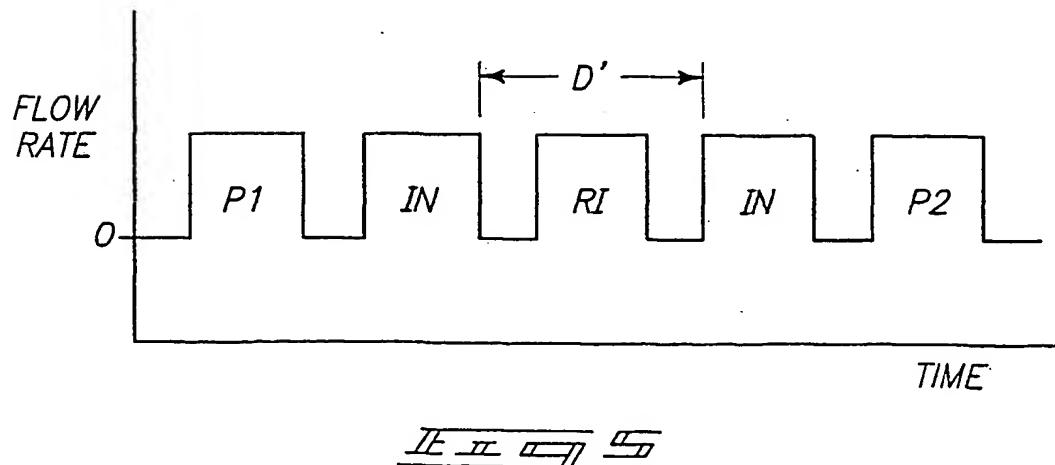
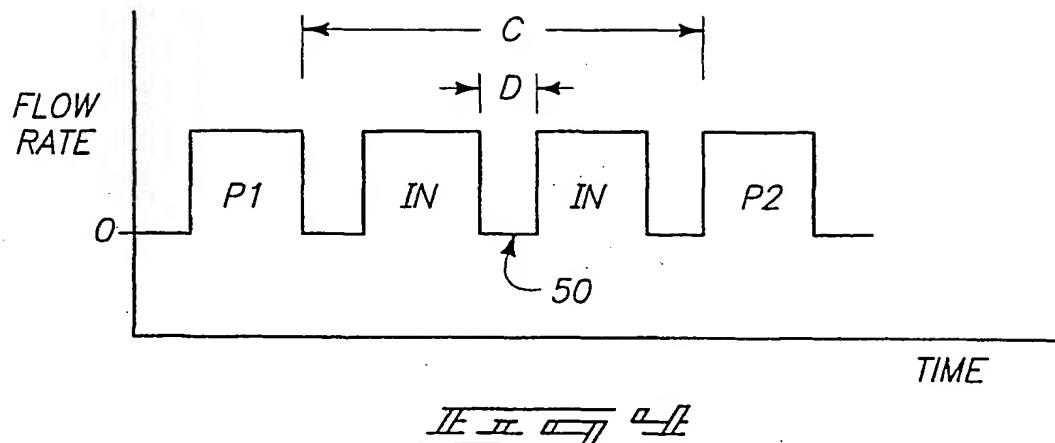
25 wherein the reactive intermediate gas is not capable of reaction with, and does not react with, any exposed portion of the substrate under said conditions during the flowing of the reactive intermediate gas.

30 54. The method of claim 44 wherein the second precursor is different in composition from the first precursor.

1/2

IE II RIIE II RI INIE II IN RI

2/2



## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 03/22804A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C23C16/44 C30B25/14

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C30B C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01 29893 A (KAIPIO SARI JOHANNA ; SOININEN PEKKA JUHA (FI); HAUCCA SUDI P (FI);) 26 April 2001 (2001-04-26) example 5	37,38
A	WO 01 27347 A (ASM MICROCHEMISTRY OY ; HAUCCA SUDI PAEIVIKKI (FI); KAIPIO SARI JOH) 19 April 2001 (2001-04-19) claims 1-6	1-54
A	US 6 200 893 B1 (SNEH OFER) 13 March 2001 (2001-03-13) claim 30	1,19,30, 37,44
A	US 2002/000598 A1 (KANG SANG-BOM ET AL) 3 January 2002 (2002-01-03) paragraph '0058!; claims 1,10	1,19,30, 37,44
		-/-

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*Z\* document member of the same patent family

Date of the actual completion of the international search

1 December 2003

Date of mailing of the international search report

09/12/2003

Name and mailing address of the ISA  
European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Cook, S

## INTERNATIONAL SEARCH REPORT

ational Application No  
PCT/US 03/22804

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2001/006835 A1 (KIM CHUNG-TAE ET AL) 5 July 2001 (2001-07-05) ---	
A	US 6 287 965 B1 (KANG SANG-BOM ET AL) 11 September 2001 (2001-09-11) column 6, line 17 - line 21; figure 1B ---	44
A	US 5 879 459 A (GADGIL PRASAD N ET AL) 9 March 1999 (1999-03-09) column 3, line 21 - line 28; figure 1B ---	44
A	WO 01 29280 A (KAIPIO SARI JOHANNA ;SOININEN PEKKA JUHA (FI); HAUKKA SUVI P (FI);) 26 April 2001 (2001-04-26) example 2 ---	1
A	US 2002/086111 A1 (BYUN JEONG SOO ET AL) 4 July 2002 (2002-07-04) paragraph '0042! ---	30,37,44
A	US 5 972 430 A (BILODEAU STEVEN M ET AL) 26 October 1999 (1999-10-26) ---	
A	WO 01 66832 A (ASM INC) 13 September 2001 (2001-09-13) -----	

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/22804

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO 0129893	A 26-04-2001	FI FI FI FI AU AU AU EP EP WO JP JP JP TW WO WO US US US US AU DE EP WO JP TW	992233 A 992234 A 992235 A 20000564 A 1088401 A 1208201 A 7925700 A 1230421 A1 1221178 A1 0127346 A1 2003511560 T 2003524888 T 2003512527 T 500826 B 0129280 A1 0129893 A1 2002187256 A1 2003031807 A1 6482262 B1 6475276 B1 7926800 A 60004566 D1 1242647 A1 0127347 A1 2003511561 T 527429 B	16-04-2001 16-04-2001 16-04-2001 16-04-2001 30-04-2001 30-04-2001 23-04-2001 14-08-2002 10-07-2002 19-04-2001 25-03-2003 19-08-2003 02-04-2003 01-09-2002 26-04-2001 26-04-2001 12-12-2002 13-02-2003 19-11-2002 05-11-2002 23-04-2001 18-09-2003 25-09-2002 10-07-2002 19-04-2001 16-04-2001 25-03-2003 19-08-2003 02-04-2003 19-04-2001 26-04-2001 26-04-2001 12-12-2002 13-02-2003 19-11-2002 05-11-2002
WO 0127347	A 19-04-2001	FI AU AU AU DE EP EP WO FI JP JP JP WO WO US US US US	992234 A 1088401 A 1208201 A 7926800 A 60004566 D1 1242647 A1 1221178 A1 0127347 A1 20000564 A 2003511561 T 2003524888 T 2003512527 T 0129280 A1 0129893 A1 2002187256 A1 2003031807 A1 6482262 B1 6475276 B1	16-04-2001 30-04-2001 30-04-2001 23-04-2001 18-09-2003 25-09-2002 10-07-2002 19-04-2001 16-04-2001 25-03-2003 19-08-2003 02-04-2003 19-04-2001 26-04-2001 26-04-2001 12-12-2002 13-02-2003 19-11-2002 05-11-2002
US 6200893	B1 13-03-2001	AU DE EP JP WO US US US US US US US US	3479100 A 1125324 T1 1125324 A1 2002539326 T 0054320 A1 2002197864 A1 2002192954 A1 2002192955 A1 2003183171 A1 6305314 B1 6475910 B1 2001000866 A1	28-09-2000 18-04-2002 22-08-2001 19-11-2002 14-09-2000 26-12-2002 19-12-2002 19-12-2002 02-10-2003 23-10-2001 05-11-2002 10-05-2001

## INTERNAL SEARCH REPORT

Information on patent family members

National Application No

PCT/US 03/22804

Patent document cited in search report	Publication date	Patent family member(s)			Publication date
US 6200893	B1	US	2001002280	A1	31-05-2001
US 2002000598	A1	03-01-2002	KR	2001066730 A	11-07-2001
			JP	2001217206 A	10-08-2001
			TW	444278 B	01-07-2001
			US	6287965 B1	11-09-2001
US 2001006835	A1	05-07-2001	KR	2001063478 A	09-07-2001
			JP	2001244263 A	07-09-2001
			TW	480622 B	21-03-2002
US 6287965	B1	11-09-2001	KR	2001066730 A	11-07-2001
			JP	2001217206 A	10-08-2001
			TW	444278 B	01-07-2001
			US	2002000598 A1	03-01-2002
US 5879459	A	09-03-1999	EP	1025278 A1	09-08-2000
			JP	2001514440 T	11-09-2001
			WO	9910558 A1	04-03-1999
			US	2002108714 A1	15-08-2002
			US	6174377 B1	16-01-2001
			US	2001011526 A1	09-08-2001
WO 0129280	A	26-04-2001	FI	992233 A	16-04-2001
			FI	992234 A	16-04-2001
			FI	992235 A	16-04-2001
			FI	20000564 A	16-04-2001
			AU	1088401 A	30-04-2001
			AU	1208201 A	30-04-2001
			AU	7925700 A	23-04-2001
			EP	1230421 A1	14-08-2002
			EP	1221178 A1	10-07-2002
			WO	0127346 A1	19-04-2001
			JP	2003511560 T	25-03-2003
			JP	2003524888 T	19-08-2003
			JP	2003512527 T	02-04-2003
			TW	500826 B	01-09-2002
			WO	0129280 A1	26-04-2001
			WO	0129893 A1	26-04-2001
			US	2002187256 A1	12-12-2002
			US	2003031807 A1	13-02-2003
			US	6482262 B1	19-11-2002
			US	6475276 B1	05-11-2002
			AU	7926800 A	23-04-2001
			DE	60004566 D1	18-09-2003
			EP	1242647 A1	25-09-2002
			WO	0127347 A1	19-04-2001
			JP	2003511561 T	25-03-2003
			AU	6800300 A	19-03-2001
			EP	1206799 A1	22-05-2002
			EP	1221177 A1	10-07-2002
			JP	2003508897 T	04-03-2003
			JP	2003531474 T	21-10-2003
			TW	478045 B	01-03-2002
			TW	478105 B	01-03-2002
			TW	527429 B	11-04-2003
			WO	0129891 A1	26-04-2001
			WO	0115220 A1	01-03-2001

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/22804

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO 0129280	A	US 2002155722 A1		24-10-2002
		US 6391785 B1		21-05-2002
US 2002086111	A1	04-07-2002	NONE	
US 5972430	A	26-10-1999	NONE	
WO 0166832	A	13-09-2001	AU 4538801 A EP 1266054 A2 JP 2003526218 T TW 490739 B WO 0166832 A2 US 2003032281 A1 US 2003129826 A1 US 2001041250 A1	17-09-2001 18-12-2002 02-09-2003 11-06-2002 13-09-2001 13-02-2003 10-07-2003 15-11-2001